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Morphology and electronic properties of the pentacene on cobalt interface

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In this paper, we report the structural and electronic properties of pentacene thin films grown on a polycrystalline Co film using atomic force microscopy and ultraviolet photoemission spectroscopy (UPS), respectively. Investigation of this type of interface is of importance for the engineering of hybrid organometallic spintronic devices for which the use of spin polarized electrodes is a prerequisite. Uniform single crystalline areas of pentacene as large as several micrometers, with molecules arranging almost perpendicular to the substrate, were obtained. For the electronic properties at this interface, we have found an energy barrier for the hole injection of about 1 eV, in spite of the fact that the ionization potential of pentacene reported previously equals the work function of Co. A shift of the vacuum level of the same magnitude has also been observed. A comparison of the UPS spectra of the pentacene films with the gas phase spectrum directly indicates that hybridization effects are present at this interface. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2363707]

INTRODUCTION

Molecular organic semiconductors have become a very active area of research during the past decade. The structural flexibility due to weak intermolecular bonds and the endless possibilities for chemical synthesis of new molecules give molecular systems a unique advantage over inorganic semiconductors for relatively simple fabrication of (opto-) electronic devices such as light emitting diodes for flexible or even transparent displays, transistors, solar cells, sensors, and solid state lasers. Applications into electronic devices in which the spin degree of freedom of the electron is exploited (spintronics) have recently started to be considered, motivated by the notion that organic semiconductors are materials with large spin relaxation times.[1–5] Spin valves with a significant magnetoresistance have been produced with Alq_3 thin films sandwiched between two ferromagnetic electrodes.[4,5]

In response to the technological success of the organic semiconductors, fundamental research, with the goal of understanding the surface and interface properties of these systems, has followed. Such studies have proven to be valuable for device engineering, as well as from the fundamental viewpoint, electronic properties of interfaces between organic semiconductors and metals being still puzzling for scientists. While the electronic and structural properties of large organic molecules on noble metals and semiconducting or semimetallic substrates have been extensively studied, only a limited number of studies on more reactive substrates, such as the ferromagnetic transition metals, have been reported.[6] Such investigations are of crucial relevance to understand and control efficient spin injection from ferromagnetic electrodes into organic thin films.

In the ferromagnetic transition metals, both the magnetic behavior and the reactivity originate from the high density of the *d* states near the Fermi level. For the structural properties it is known up to now that deposition of organic molecules on reactive substrates, such as ferromagnetic transition metals, leads mostly to disordered structures.[7,8] In some cases, because of the high reactivity of the substrate molecules decompose at temperatures below room temperature.[8–11] For this class of substrates it has been shown though that bonding to the substrate and hence the molecular order can be influenced by changing the type of the molecule or by passivating the substrate.[8,12,13] An example of a stable interface is that of C_{60}/Ni(110),[14,15] with a decomposition temperature of C_{60} around 850 K. A strong interaction has been reported in the latter case as well.

In this paper we present the structural and electronic properties of the interface between pentacene and Co. Pentacene is one of the semiconducting organic materials with a high charge carrier mobility.[16–20] For the structural properties of this particular interface, we will show that pentacene forms ordered domains when deposited at elevated temperatures on polycrystalline Co films, with an almost perpendicular orientation of the molecules to the substrate. Because of the large ordered areas formed on the polycrystalline substrate, one would not expect a very strong interaction to take place. The study of the electronic properties of the pentacene-cobalt interface is even more interesting since the work function of Co (5 eV) is closed to the ionization potential of pentacene, for which values from 4.9 to 5.2 eV have been reported.[21–23] If no chemical interaction takes place and

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the vacuum levels align at this interface, one would expect therefore a very small hole injection barrier at the pentacene-cobalt interface. Contrary to our expectations, we show in this work that the vacuum level of pentacene does not align to that of Co, consistent with the formation of an interfacial dipole layer with the positive part at the pentacene side. As a consequence, the barrier for the hole injection is also higher than expected. We attribute these observations to strong hybridization effects, which is to be seen in the creation of interface states in the gap of the organic semiconductor and in shifts of the topmost molecular orbitals that overlap with the 3*d* band of Co.

EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) system with a base pressure of 2×10^{-10} mbar. The system was equipped with ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), and a preparation chamber with deposition facilities. As substrates for our organic layers, we used clean polycrystalline Co films (100 Å thick), which were deposited by thermal evaporation on silicon substrates with a natural oxide. The silicon substrates were carefully cleaned by sonication in ammonia, acetone and ethanol, and outgassed in UHV for several hours. Tantalum buffer layers were used to decrease the roughness of the Co layer.

Pentacene was purchased at Aldrich company and further purified by gradient sublimation at 10^{-6} mbar. The purified material was then inserted in the preparation chamber in a glass crucible which was resistively heated at temperatures between 480 and 510 K. Before evaporation the material was carefully outgassed for several days and continuously held at a temperature that was 50° lower than the evaporation temperature. The pressure during evaporation of pentacene never exceeded 8×10^{-10} mbar. The evaporation rate was determined as follows. A tantalum ribbon of 0.25 μm thickness attached to the SiO_x substrates was used as a mask for the deposition of pentacene, the surface underneath remaining uncovered. After deposition, the ribbon was removed and the profile at the edge between the covered and uncovered regions was measured with an atomic force microscope (AFM). The height of the step measured in this way was used for further calibration of a quartz crystal microbalance.

The morphology of the pentacene films was determined *ex situ* immediately after the film was taken out of the vacuum, using soft tapping mode AFM.

For the UPS studies a He I gas discharge lamp having a main line of 21.22 eV was used, with a satellite of 1.86 eV higher in energy and an intensity lower than 2% of the main line. In this study, we have used XPS, with a nonmonochromatic Al $K\alpha$ x-ray source (1486.6 eV), to check the cleanliness of the sample. The photoelectrons were analyzed with a hemispherical analyzer from Vacuum Generators. The angle of incoming light was 35° from the surface normal; the outgoing electrons were collected under an angle of 35° with respect to the surface normal. The experimental resolution, determined from the Ag Fermi edge was 1.5 eV for XPS and 0.15 eV for UPS. The UPS spectra were recorded with a negative bias of 4 V applied on the sample in order to register the secondary electron cutoff. All the UPS spectra presented in this work are satellite corrected. The spectra were analyzed using the WINSPEC program, developed in the LISE laboratory of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium. We mention also that no change in time was registered in the spectra, which means that the pentacene layers were not degraded by the ultraviolet source used for the UPS experiments.

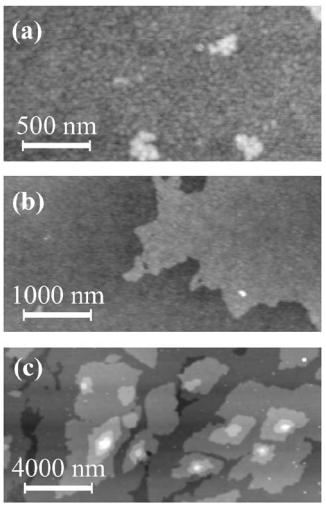

FIG. 1. Morphology of thin pentacene layers deposited on polycrystalline Co films.

The gas phase spectra were measured in a separate vacuum chamber with a base pressure of 2×10^{-7} mbar. The excitation source for the gas phase photoemission experiments was a high intensity source from Omicron (HIS 13) and the photoelectrons were analyzed with a homemade hemispherical analyzer equipped with three channeltrons. The binding energy of the molecular levels was precisely determined by referencing the spectra to that of Xe, which has two well known lines $^2P_{3/2}$ and $^2P_{1/2}$ at 12.13 and 13.44 eV, respectively.

RESULTS AND DISCUSSION

Structural properties

We analyzed the morphology of pentacene layers deposited on polycrystalline Co thin films as a function of substrate temperature and evaporation rate. At elevated temperatures we observed a tendency of forming domains with well defined shapes, indicating that well ordered structures are formed.

Selected AFM micrographs of pentacene films for various film thicknesses ranging from the submonolayer regime up to 1.7 MLs are (monolayer) shown in Fig. 1. The films were grown on a substrate temperature of 300 K with an evaporation rate of 1 Å/min. For a nominal coverage of approximately 3 Å, as shown in Fig. 1(a), islands with a density of approximately 0.08 μm^{-2} and a height of 20 to 90 Å are formed. Because the height of the islands is bigger than the length of one pentacene molecule (18 Å), we conclude

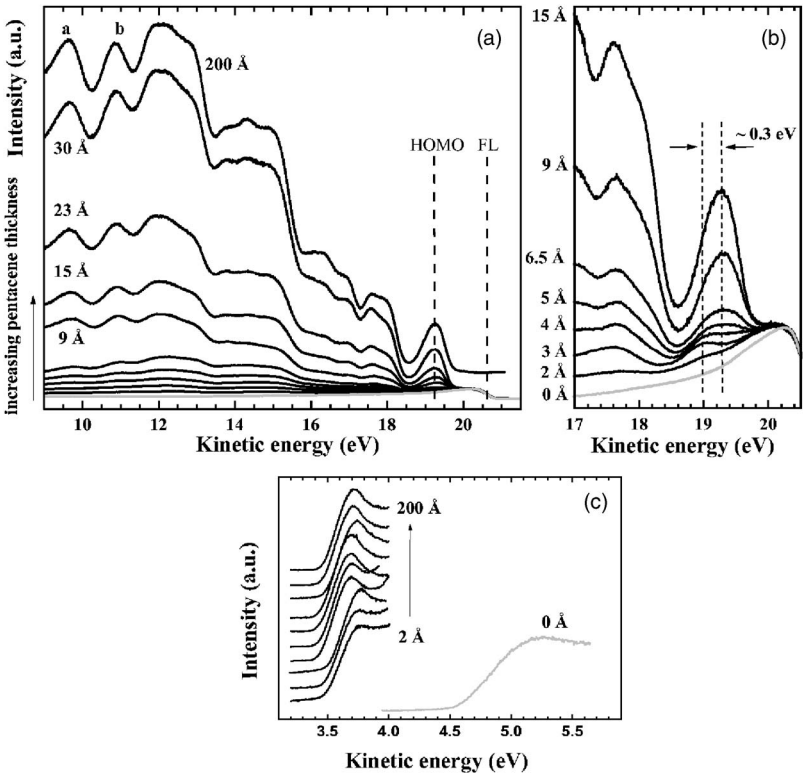

FIG. 2. (a) Valence band photoemission spectra at the pentacene-cobalt interface; (b) close up into the spectral region around HOMO for small amounts of pentacene; (c) secondary electron cutoff part of the UPS spectra.

that at this stage the molecules have a random orientation. The nucleation starts presumably at defects or impurities, similar to the case of SiO_x substrates.[24]

At higher coverages, the molecules form large uniform covered areas. For example, the AFM picture for a pentacene nominal coverage of 7 Å shown in Fig. 1(b) reveals the existence of two height levels, which correspond to the Co (left side of the image) and the pentacene terrace, respectively (right side of the image). The average value of the step height for the first layer of 15±3 Å is comparable to the well known thin-film phase formed on SiO_x for which the plane spacing $d(001)$ is reported to be 15.4 Å.[20] This would correspond to an almost perpendicular orientation of the molecules on the substrate. From the well defined shape of the area covered with pentacene, we can conclude that the pentacene film is ordered. Terraces with a lateral size as large as 5 μm are observed for this coverage.

We mention that the morphology and the roughness of the pentacene covered region are the same with those of the underlying substrate. In the AFM micrograph corresponding to nominal coverages of 27 Å [Fig. 1(c)], areas at six different height levels are observed, showing that the second to fifth layers formed before the first layer are completely closed. The nucleation of the second layer (not shown here) starts above a nominal coverage of 7 Å. A line scan through different terraces (see also Ref. 13) reveal a height difference of approximately 15±3 Å, indicating that pentacene keeps its perpendicular orientation on the substrate. The size of the crystalline domains depends on the evaporation conditions and also on the roughness of the underlaying substrate. Increased substrate temperatures and decreased evaporation rates lead to an increased domain size. An increase in the size of the terraces has also been observed when the roughness of the Co films was decreased. The root mean square (rms) roughness of the Co film used for the samples shown in Fig. 1 is 3 Å. For the UPS studies presented in the following section, we have used polycrystalline Co films with a rms roughness of 5 Å.

Electronic properties

In order to assess the electronic structure at the pentacene-cobalt interface, we measured the photoemission spectra for different thicknesses of pentacene. To avoid differences in work function of the substrate from one sample to another, we deposited the pentacene films subsequently in small amounts on the same Co substrate. After each step of deposition, the UPS spectrum was recorded. During deposition, the substrate was kept at a temperature of 345 K.

The photoemission spectrum of Co is denoted by "0 Å" in Fig. 2. This spectrum consists only of a peak around a kinetic energy of 20.5 eV, characteristic of the occupied 3*d* and 4*s* bands, which dominate the region near the Fermi level. The work function of Co can be determined from the UPS spectra by subtracting the width of the spectra (defined between the Fermi level cutoff and the secondary electron cutoff) from the photon energy of the incoming light.[6,25] We found a value of 5.1 eV. Within the experimental resolution, the work function found is in good agreement with previous published values.[26]

We next turn to the UPS spectra corresponding to pentacene films of different thicknesses. Figure 2(b) represents a close-up in the UPS spectra for thicknesses of pentacene up to 15 Å. For small amounts of pentacene, both Co and pentacene contribute to the measured spectrum. Spectral features originating from the density of states at the Fermi level of Co

are observed up to a thickness of 45 Å (~3 MLs of molecules arranged perpendicularly on the substrate). In order to elucidate the modification in the valence band UPS spectra during film growth, we normalized the measured spectra with respect to the intensity at 20.27 eV. This value corresponds to the maximum intensity of the Co 3*d* band. The molecular orbitals of pentacene are visible at kinetic energies below 20 eV. The signal originating from the highest occupied molecular orbital (HOMO) level is found at kinetic energies around 19.4 eV. The signature of molecular orbitals of pentacene appears already at very low coverages.

The spectral region around the secondary electron cutoff (SEC) for different amounts of pentacene is represented in Fig. 2(c). For the clean Co layer the SEC corresponds to 4.6 eV. A sudden change of −1 eV in the SEC occurs at the very first layer of pentacene with a thickness of 2 Å. This shift corresponds to the formation of an interfacial dipole with the positive charge at the pentacene side. The dipole barrier results in a vacuum level misalignment and would, in principle, result in a rigid shift of the pentacene molecular orbital structure with respect to the Co density of states. This would create a gap between the HOMO of pentacene and the Fermi level of Co of Ca. 1 eV, which would represent the effective hole injection barrier. We found that the barrier for hole injection is very sensitive to small amounts of impurities in the Co layer, with the barrier decreasing as the amount of impurities was increased.

To asses the origin of the interfacial dipole, we have to analyze more closely the valence band spectrum. The most significant modification in the spectrum appears in the region around the highest occupied molecular orbital of the pentacene, as is visualized in Fig. 2(b). For clarity, we show in this figure only the spectra corresponding to pentacene thicknesses up to 15 Å, since most of the modification in the spectra happens in the submonolayer regime. In this figure we observe upon deposition of the first monolayer of pentacene an increase of the binding energy of the HOMO by 0.3 eV with respect to the bulk value. The binding energy of the HOMO relaxes to the bulk value as the amount of pentacene increases to about 7 Å. The change in the HOMO binding energy in the proximity of the Co substrate is indicative of hybridization between the pentacene frontier orbitals and the Co 3*d* orbitals.

More detailed analyses of the spectral features around the Fermi edge at submonolayer coverage reveal additional spectral weight which cannot be attributed to pure pentacene or Co orbital features. This extra spectral weight, which may originate from new states formed in the HOMO-lowest unoccupied molecular orbital (LUMO) gap of the pentacene molecules at the interface, is revealed by subtracting the Co spectrum from the spectrum of a thin layer of pentacene on Co (see lower part of Fig. 3). The fact that the spectra corresponding to thin films differ from the multilayer ones is attributed to hybridization of the molecular levels that overlap with the 3*d* band of Co. We conjecture that the increased spectral weight at the high kinetic energy side of the HOMO of pentacene should be attributed to the formation of interface states. More detailed investigations would be required to identify the exact nature of these states.

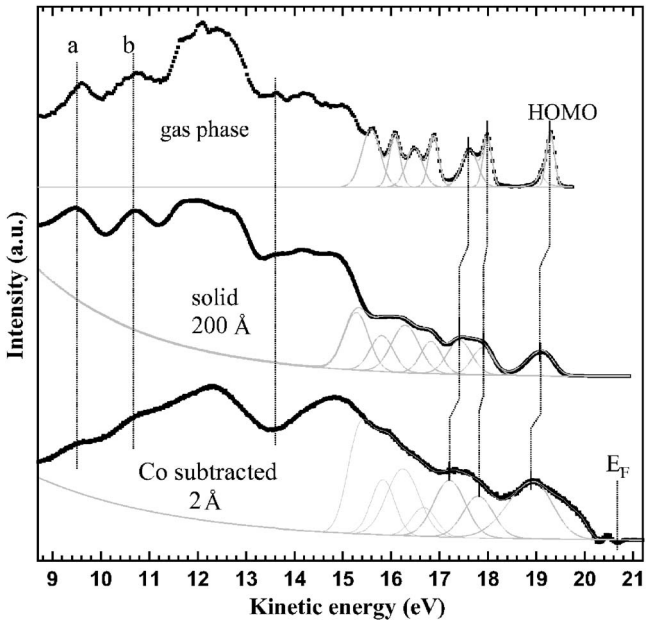

FIG. 3. Gas phase UPS spectrum of pentacene (top) together with UPS spectra of thin films of pentacene. The thickness of the pentacene layers are indicated. The UPS spectrum of Co was subtracted from the 2 Å spectrum.

Besides the modification in the spectra around the HOMO of pentacene, other levels are found to be shifted. We display in Fig. 4 the shifts registered for HOMO, HOMO-1, and HOMO-2 and the peaks labeled as "a" and "b" in Fig. 2(a). We note that the contribution to the a and b peaks comes from σ orbitals. In order to derive the exact positions of the other molecular orbitals, we had to rely on a fit of the UPS spectra. We used peaks with a Gaussian shape. In the solid state spectrum we fitted the HOMO peak with an asymmetric shape. The position of the deeper lying a and b peaks are determined at the maximum intensity of these peaks. The fitting procedure indicates that for the 2 Å coverage, the HOMO-1 and HOMO-2 peaks are about 0.2 eV broader than in the multilayer case.

In Fig. 4, we can see that for the 2 and 3 Å spectra, the peaks shift in the same direction, but by different amounts.

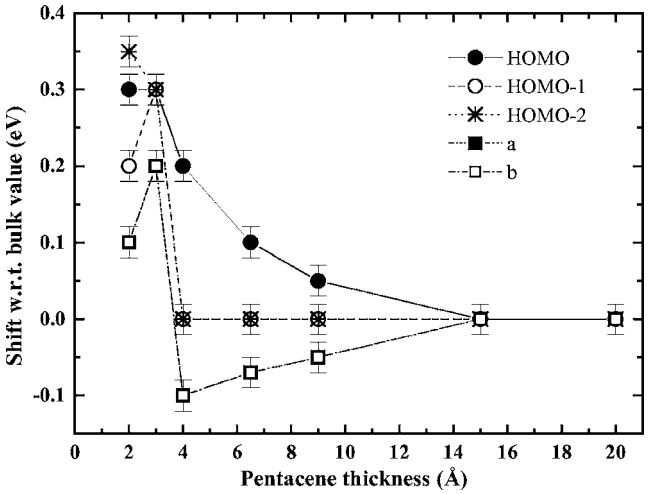

FIG. 4. Shifts of the molecular levels for different layers of pentacene, with respect to those of a thick pentacene layer. The levels labeled "a" and "b" are defined in Fig. 2(a).

However, in the 4 Å spectrum we can see that different levels shift differently. Beyond a thickness of 4 Å, the shifts gradually decreases, and at a thickness of about 15 Å they become zero. With a drastic change in the a and b, HOMO-1 and HOMO-2 peaks occur therefore at thicknesses around 4 Å.

The sudden change in the spectra around 4 Å can originate from two effects. One possibility is that the molecules adopt a different orientational conformation in the very early stage of growth. The other possibility is that pentacene starts to nucleate at step edges, defect sites, or grain boundaries of the Co film. For the first hypothesis, we refer to the case of the pentacene Au(111) interface for which it has been shown that the molecules adopt in the earliest stage of growth a flat orientation on the substrate.[27] The pentacene starts to tilt out of the plane only after completion of the first monolayer of flat laying molecules. This coverage would correspond to a thickness around 3 Å. In the case of a flat orientation there is a much larger overlap between the π orbitals and the substrate than in the case of a perpendicular orientation. This would result in different features in the electronic structure than for the perpendicular orientation. In the other hypothesis, we assume that the molecules gather first in nucleation points at defects, and only after a 4 Å coverage do they start to diffuse. At these defects, a stronger interaction of pentacene is expected. In fact, we cannot exclude the possibility that the molecules adopt within such a cluster an orientation mostly with the molecular plane parallel to the substrate at the very early stage of nucleation. Our AFM images for low pentacene coverages (see Fig. 1) indicate that the molecules cluster in small nucleation points of up to 90 Å in height, rather than distribute uniformly on the substrate. This would exclude in fact the formation of the flat lying monolayer of pentacene.

Finally, we address the difference between the gas phase and solid state UPS spectra of pentacene. We have compared the UPS spectra of thin films with the UPS gas phase spectra (light gray in Fig. 3). Since we do not expect any hybridization effects at the deep lying levels, we have aligned all the spectra such that the levels at the 10.8 eV overlap in all spectra. In the UPS spectra of 200 Å of pentacene we can distinguish shifts in the HOMO, HOMO-1, and HOMO-2 with respect to the gas phase. Furthermore, all features in the thin film phase are broadened. A similar broadening of the HOMO, for instance, has been registered in the case of the pentacene-samarium system, for which a weak interaction with the substrate has been reported.[22] This means actually that the broadening and the shift we observe in the spectra of the thick pentacene film with respect to the gas phase spectra are due to charge redistribution caused just by the interaction between the molecules themselves.

For the ionization potential of pentacene in the gas phase we measured a value of 6.44 eV, which we determined from the cutoff of the HOMO at the high kinetic energy side. The ionization potential in the solid state phase of 5.0 eV was determined by subtracting the width of the whole UPS spectra of a thick pentacene film (defined from the secondary cutoff till the high kinetic energy cutoff) from the photon energy. The difference in the two ionization potentials corresponds to the polarization energy in solid pentacene.

We point out that in Fig. 3 the value for kinetic energy is arbitrary because of the shifts we applied to the spectra. We have indicated instead the position of the Fermi level (FL) for the spectra corresponding to thin films of pentacene. Small intensity variations in the subtracted spectrum around the FL occur because the spectra do not completely overlap at the Fermi edge just due to measurement errors. For the spectrum corresponding to small amounts of pentacene, a shift of the HOMO, larger than in the multilayer case, is observed as explained before.

CONCLUSIONS

In summary, we presented the structural and electronic properties of pentacene films deposited on polycrystalline Co substrates. We have shown that deposition of pentacene on Co at elevated substrate temperatures leads to the formation of uniform ordered areas of several micron size, with molecules arranged almost perpendicular to the substrate. The electronic properties of this interface were analyzed by means of the UPS technique. Despite the fact that the work function of Co is very close to the ionization potential of pentacene, we measured at the interface of these two systems a barrier for the hole injection in the order of 1 eV. This observation is of profound interest for engineering of organic spin-valve devices.[4,5] A vacuum level shift of 1 eV was found at the interface, which indicates the formation of an interfacial dipole with the positive part at the pentacene side. The origin of the dipole can be attributed to a redistribution of charge at the interface by hybridization between the pentacene frontier orbitals and the Co 3*d* band and to the formation of intergap states. Furthermore, we compared the gas phase spectrum with the solid phase spectrum of thin films of pentacene. We found a difference of 1.4 eV between the ionization potential in the two phases, which we attribute to the change in the local environment and hybridization effects between pentacene molecules.

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